

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE November 16, 1998	3. REPORT TYPE AND DATES COVERED Technical Report # 29		
4. TITLE AND SUBTITLE Efficient Xerographic Photoreceptors from Conjugated Polymers and Polymer Blends.		5. FUNDING NUMBERS N00014-94-1-0540 Kenneth J. Wynne R & T Code 3132111		
6. AUTHOR(S) Xuejun Zhang, Anita K. Alanko, and Samson A. Jenekhe				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Rochester Department of Chemical Engineering 206 Gavett hall, Box 270166 Rochester, NY 14627-0166		8. PERFORMING ORGANIZATION REPORT NUMBER # 29		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES Proc. SPIE- International Society of Optical Engineers, 3144, 41-52 (1997).				
a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.		12. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Bilayer xerographic photoreceptors in which π -conjugated polymers and binary conjugated polymer blends are used as the charge generation layer have been fabricated, evaluated, and shown to be highly efficient. Devices incorporating poly(1,4-phenylene benzobisthiazole), poly(2,5-pyridylene benzobisthiazole), poly(1,4-phenylenebisvinylene benzobisthiazole), poly(1,4-(2-hydroxy)phenylene benzobisthiazole), and poly(benzimidazobenzophenanthroline ladder) as the charge generation layer and a layer of tris(<i>p</i> -tolyl)amine (TTA) dispersed in polycarbonate as the charge-transport layer showed good photosensitivities (6–18 ergs/cm ²), good dark decay characteristics (2–10 V/s at surface potentials of 400–600 V), and high charge generation quantum efficiencies (20–50% at $\sim 10^6$ V/cm). Photoreceptors using binary blends of conjugated polymers had enhanced spectral range of photosensitivity (300–700 nm) and significantly enhanced quantum yield for charge photogeneration relative to the component conjugated polymers. Photocarrier generation in these bilayer photoreceptors is <i>extrinsic</i> in nature and is mediated by exciplex formation between the conjugated polymer and TTA at the bilayer interface. Observed nanoscale size effects, in which the photoreceptor performance (quantum efficiency, photosensitivity) is enhanced with decreasing size of the charge generation layer, provide a means of tuning the photoconductive properties of optoelectronic devices based on conjugated polymers. A model derived from Onsager's 1934 theory was used to estimate the primary quantum yield of ion-pairs and ion-pair separation distance in the bilayer photoreceptors to be 0.21–0.62, and 4–6 Å, respectively.				
14. SUBJECT TERMS Xerographic photoreceptors; conjugated polymers; polymer blends; charge photogeneration; nanoscale size effects.		15. NUMBER OF PAGES 12		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

19981120 173

OFFICE OF NAVAL RESEARCH

GRANT NO: N00014-94-1-0540

R&T Code 3132111

Kenneth J. Wynne

Technical Report NO. 29

Efficient Xerographic Photoreceptors from Conjugated
Polymers and Polymer Blends

By

Xuejun Zhang, Anita K. Alanko, and Samson A. Jenekhe

Prepared for Publication

In

Proc. SPIE-International Society of Optical Engineers

Department of Chemical Engineering and
Center for Photoinduced Charge Transfer
University of Rochester, New York 14627

November 16, 1998

Reproduction in whole or in part is permitted for any purpose
of the United States Government

This document has been approved for public release and sale;
its distribution is unlimited.

Efficient xerographic photoreceptors from conjugated polymers and polymer blends

Xuejun Zhang, Anita K. Alanko, and Samson A. Jenekhe

Departments of Chemical Engineering and Chemistry and Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York 14627-0166

ABSTRACT

Bilayer xerographic photoreceptors in which π -conjugated polymers and binary conjugated polymer blends are used as the charge generation layer have been fabricated, evaluated, and shown to be highly efficient. Devices incorporating poly(1,4-phenylene benzobisthiazole), poly(2,5-pyridylene benzobisthiazole), poly(1,4-phenylenebisvinylene benzobisthiazole), poly(1,4-(2-hydroxy)phenylene benzobisthiazole), and poly(benzimidazobenzophenanthroline ladder) as the charge generation layer and a layer of tris(*p*-tolyl)amine (TTA) dispersed in polycarbonate as the charge-transport layer showed good photosensitivities (6–18 ergs/cm²), good dark decay characteristics (2–10 V/s at surface potentials of 400–600 V), and high charge generation quantum efficiencies (20–50% at $\sim 10^6$ V/cm). Photoreceptors using binary blends of conjugated polymers had enhanced spectral range of photosensitivity (300–700 nm) and significantly enhanced quantum yield for charge photogeneration relative to the component conjugated polymers. Photocarrier generation in these bilayer photoreceptors is *extrinsic* in nature and is mediated by exciplex formation between the conjugated polymer and TTA at the bilayer interface. Observed nanoscale size effects, in which the photoreceptor performance (quantum efficiency, photosensitivity) is enhanced with decreasing size of the charge generation layer, provide a means of tuning the photoconductive properties of optoelectronic devices based on conjugated polymers. A model derived from Onsager's 1934 theory was used to estimate the primary quantum yield of ion-pairs and ion-pair separation distance in the bilayer photoreceptors to be 0.21–0.62, and 4–6 Å, respectively.

Keywords: photoreceptors; conjugated polymers; polymer blends; charge photogeneration; nanoscale size effects.

INTRODUCTION

Organic photoconductive materials are currently used as photoreceptors in electrographic imaging systems such as photocopiers, laser printers, and fax machines.^{1,2} Such organic photoreceptors are typically bilayer devices in which one layer serves as the charge generation layer (CGL) and the other layer serves as the charge transport layer (CTL). Current CTL materials are typically triarylamine molecules dispersed in an inert polymer matrix.^{1,3,4} Since the development of hole-transport materials is more advanced than that of electron-transport materials, current commercial organic photoreceptors are fabricated with CTL materials that transport holes.^{1,5} Current organic CGL materials include metallophthalocyanines, perylene pigments, squaraines, and azo compounds dispersed in polymer matrices.² Such dye molecule-doped polymer systems are in general metastable materials that are subject to phase separation and crystallization over time, reducing the long-term stability and performance of photoreceptors. We recently explored π -conjugated polymers as *single-component* CGL materials in xerographic photoreceptors.^{6–9} Conjugated polymers have also been shown to be promising materials for other optoelectronic applications such as photodiodes, photovoltaic cells, and light-emitting diodes.¹⁰ Key to many of these applications are the processes of generation, injection, transport, and recombination of charge carriers in the materials. This paper focuses on the photoconductive properties, particularly charge photogeneration phenomena, in π -conjugated polymers

in the context of developing the materials for electrophotographic imaging and other optoelectronic applications.

Intrinsic photoconductivity of conjugated polymers has been previously studied in polyacetylene,¹¹ polydiacetylenes,¹² poly(phenylene vinylenes),¹³ poly(3-alkylthiophenes),¹⁴ and polyquinolines.¹⁵ Extrinsic photoconductivity of conjugated polymers has also been reported in polymer-C₆₀ heterojunctions,^{10(a)} polymer-C₆₀ composites,¹⁶ polymer-polymer blends,¹⁷ and bilayer assemblies of n-type conjugated polymers with triaryl amines.⁶⁻⁹ It was found that in these conjugated polymer systems, photoinduced electron transfer played a critical role in the enhancement of extrinsic photoconductivity compared to the intrinsic photoconductivity of the pure polymers. For example, enhanced charge photogeneration in bilayer photoreceptors using conjugated polymers was previously reported by our laboratory.⁶⁻⁹ In such bilayer photoreceptor devices, conjugated polymers were used as the charge-generation layer (CGL) and a molecularly-doped-polymer TTA:PC [tris(*p*-tolyl)amine):polycarbonate] was employed as the charge-transport layer (CTL). The TTA:PC system has been shown to be a trap-free hole transporting material.³ A variety of experimental measurements including photogeneration quantum efficiency as a function of electric field, picosecond photoinduced absorption, and steady-state and time-resolved photoluminescence spectroscopy on the bilayer devices suggested that exciplex formation between the n-type conjugated polymer (acceptor) and TTA (donor) plays a critical role in the process of charge photogeneration.⁶⁻⁹

In this paper, we report the fabrication and evaluation of bilayer photoreceptors using n-type (electron transporting) conjugated polymers, such as poly(1,4-phenylene benzobisthiazole) (PBZT), poly(1,4-phenylenebisvinylene benzobisthiazole) (PBTPV), poly(2,5-pyridylene benzobisthiazole) (PPyBT), poly(1,4-(2-hydroxy)phenylene benzobisthiazole) (HPBT), and poly(benzimidazobenzophenanthroline ladder) (BBL) as the charge generation layer and tris(*p*-tolyl)amine doped polycarbonate (TTA:PC) as the charge transport layer. Quantum efficiency of charge photogeneration in these photoreceptors was measured at electric fields of 10⁴–10⁶ V/cm by applying the xerographic photodischarge technique. It is shown that the performance of the conjugated polymer-based bilayer devices (dark decay, photosensitivity, and quantum efficiency) is comparable to commercial organic photoreceptors.^{1,2} The primary quantum yield of ion-pairs ϕ_0 and the ion-pair separation distance r_0 in the new photoreceptors were obtained from the measured electric field dependent charge photogeneration efficiency by a theoretical model²⁴ developed with the aid of Onsager's 1934 theory.²⁵ Nanoscale size effects on photogeneration in bilayer photoreceptors was also explored by varying the thickness of the conjugated polymer CGL. Finally, we report on initial studies aimed at the enhancement of photogeneration quantum efficiency and the spectral range of photosensitivity in bilayer photoreceptors by using conjugated polymer blends as the CGL.

EXPERIMENTAL SECTION

Materials. The molecular structures of the conjugated polymers, TTA, and polycarbonate used to fabricate xerographic photoreceptors are shown in Figure 1. The synthesis and detailed characterization of the conjugated polymers used in our studies have been reported elsewhere: PBZT,^{20(a),20(b)} PBTPV,^{20(b),20(c)} PPyBT,^{20(d),20(e)} HPBT,^{20(f)} BBL.^{20(g)} Polycarbonate and TTA were provided by Eastman Kodak company and used without further purification.

Device Fabrication. Bilayer photoreceptors consisting of a thin layer (9–195 nm) of a conjugated polymer and a thick layer (10–22 μ m) of a trap-free tris(*p*-tolyl)amine (TTA) doped polycarbonate (TTA:PC) were used in our studies. The bilayer devices were fabricated on a Ni-coated poly(ethylene terephthalate) (PET) substrate (Figure 2). The molecularly-doped polymer system TTA:PC is known to be a trap-free material,³ which means that charges photogenerated or injected into it can move through it over long distances without being trapped. In the case of TTA-doped polycarbonate used here, it is a trap-free *hole* transport material.³

The Lewis acid coordination complexation method²¹ was used to prepare isotropic solution of each conjugated polymer or polymer blend in nitromethane containing aluminum chloride (AlCl₃) or gallium chloride (GaCl₃). Bilayer devices on which photodischarge measurements were performed were prepared by spin coating a solution of the conjugated polymer onto nickel-coated PET substrates. The pure polymer

films were obtained by regeneration of the polymer-Lewis acid complex in deionized water.²¹ The polymer films obtained were vacuum dried at 80 °C overnight and were subsequently overcoated with a TTA:PC layer. The TTA:PC layer was in the ratio of 40:60 by weight and was blade coated from a dichloromethane solution and dried in vacuum at 40 °C overnight. The films for the absorption measurement were prepared on silica substrates by following the same procedures described above. Polymer film thicknesses were measured by using a profilometer (Tencor Instruments, Model 200 Alpha-step) and by an optical technique based on the known absorption coefficients of the polymers.

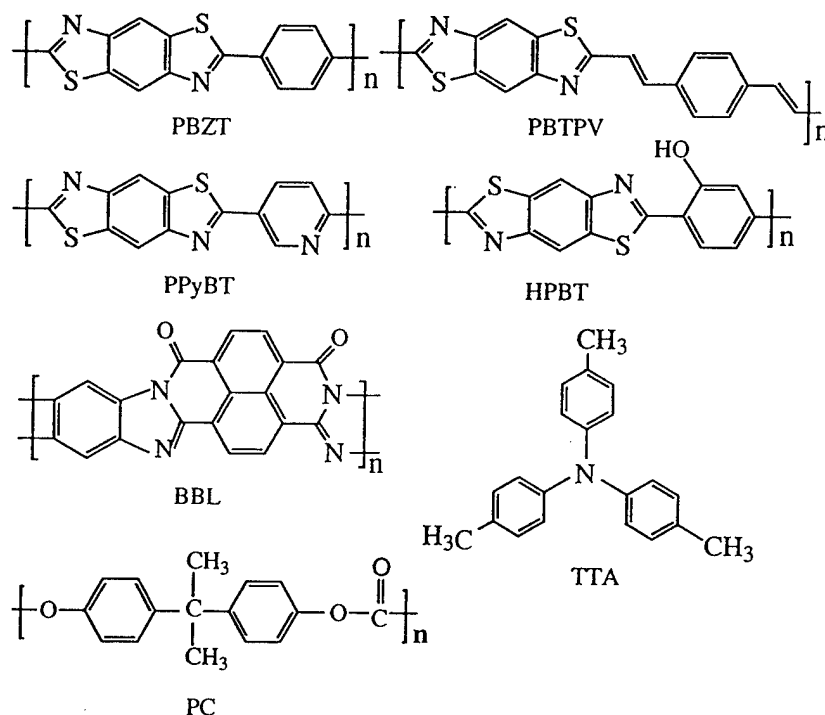


Figure 1. Chemical structures of the materials used in this study.

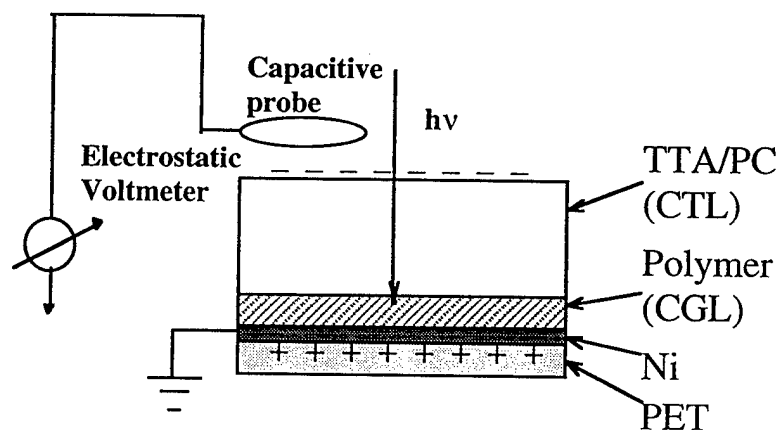


Figure 2. Schematic of a conjugated polymer photoreceptor.

Evaluation of Devices. Optical absorption spectra were obtained with a Perkin Elmer Model Lambda 9 UV-vis-near IR spectrophotometer. Details of the xerographic photodischarge equipment and its use for measurement of charge photogeneration were described previously.⁷ The bilayer device shown in Figure 2 was mounted in a xerographic cycling chamber designed so that either a corona charger or a Monroe Electronics Model 114S-4 electrostatic voltmeter detector can be positioned in front of the sample. The device was charged to the desired surface potential (negative) with a corona charger supplied by a Universal Voltronics high-voltage source. An electrostatic voltage detector placed in front of the device measured the surface potential. A photoreceptor device under test was illuminated by a 45-watt tungsten lamp passing through a Bausch and Lomb monochromator. The intensity of the exposing radiation was kept low (2~2.5 ergs/cm²) to minimize space charge effects. The resulting photodischarge data were acquired using a computer program. The quantum efficiency for charge photogeneration was determined from the initial rate of discharge of the device.²²

$$\phi = \frac{\epsilon\epsilon_0}{eI} \left(\frac{dV}{dt} \right)_{t=0} \quad (1)$$

where ϵ is the dielectric constant, ϵ_0 the permittivity of free space, e the electronic charge, l the bilayer film thickness, I the light intensity absorbed, V the surface potential, and t the time. The field across the device was taken as V/l , and the exposure time was set to be 1.2 s. The bilayer film thickness for all the photoreceptors investigated was in the range of 10 to 22 μm . All measurements were made at room temperature ($\sim 22^\circ\text{C}$).

RESULTS AND DISCUSSION

Optical Absorption Spectra. Figure 3 shows the optical absorption spectra of single-layer thin films of PBZT, PBTPV, PPyBT, HPBT, and BBL on silica substrates. The strong absorption bands of these conjugated polymers in the visible range meet the spectral requirement for photoreceptors in copier applications.² The optical absorption lineshapes of PBZT, PBTPV, PPyBT, and HPBT are very similar because of their general structural similarity as members of conjugated polybenzobisthiazoles. However, due to the different linkages in the polymer backbone, the absorption maximum varies. PBZT and PPyBT have two absorption maxima around 440 and 470 nm in the visible. Those of HPBT are red shifted to 450 and 480 nm. The absorption maxima of PBTPV are further red shifted to 480 and 515 nm. The conjugated ladder polymer BBL has a broad visible absorption with a maximum around 565 nm. The absorption band of TTA:PC film was below 350 nm and not shown. In the photogeneration experiments, the longer wavelength absorption maximum was chosen as the illumination wavelength for each polymer CGL. Therefore, the incident light will only be absorbed by the conjugated polymer layer. We also found that the optical absorption spectrum of each conjugated polymer/TTA:PC bilayer investigated was a superposition of the absorption bands of the conjugated polymer and TTA:PC layers. No new absorption band was observed in the 200 to 3200 nm spectral range, indicating that the conjugated polymer and TTA do not form observable charge transfer complex in the ground state.

Charge Photogeneration in Photoreceptors. Two representative photoinduced discharge curves for HPBT/TTA:PC (80-nm HPBT, 480-nm illumination) and PPyBT/TTA (33-nm PPyBT, 470-nm illumination) bilayer devices are shown in Figure 4. The devices were charged to a surface potential of ~ 490 V. Three important device parameters, i.e. photosensitivity, dark decay, and residual potential, were obtained from the discharge curves. For the PPyBT/TTA bilayer device, the photosensitivity was ~ 6 ergs/cm², the dark decay was ~ 5 V/s and the residual potential was ~ 20 V. The HPBT/TTA:PC device showed a photosensitivity of ~ 15 ergs/cm², a dark decay of ~ 10 V/s, and a residual potential of ~ 20 V. The performance of photoreceptors made from different conjugated polymers is listed in Table 1. All the devices showed a residual potential of about 20 V, dark decay of 2-10 V/s, and photosensitivity of 6-18 ergs/cm². These device properties are comparable to those reported for current organic photoconductive materials.²

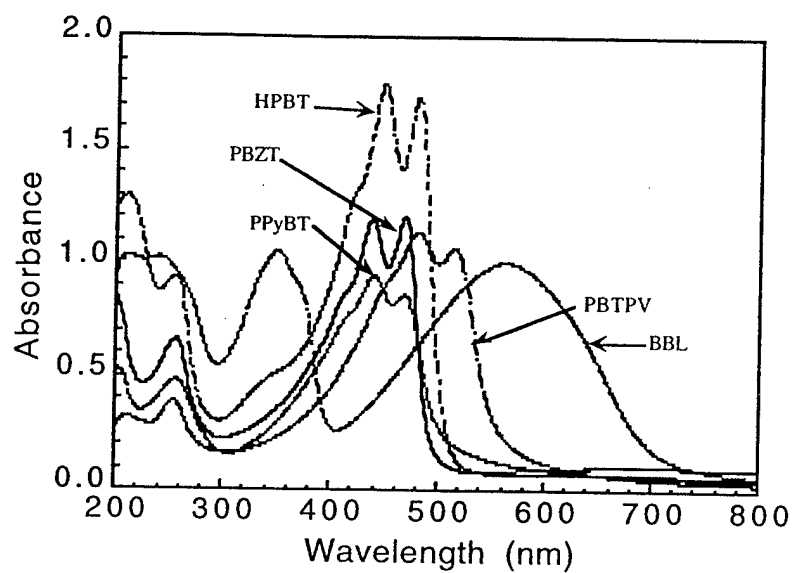


Figure 3. Optical absorption spectra of conjugated polymer thin films.

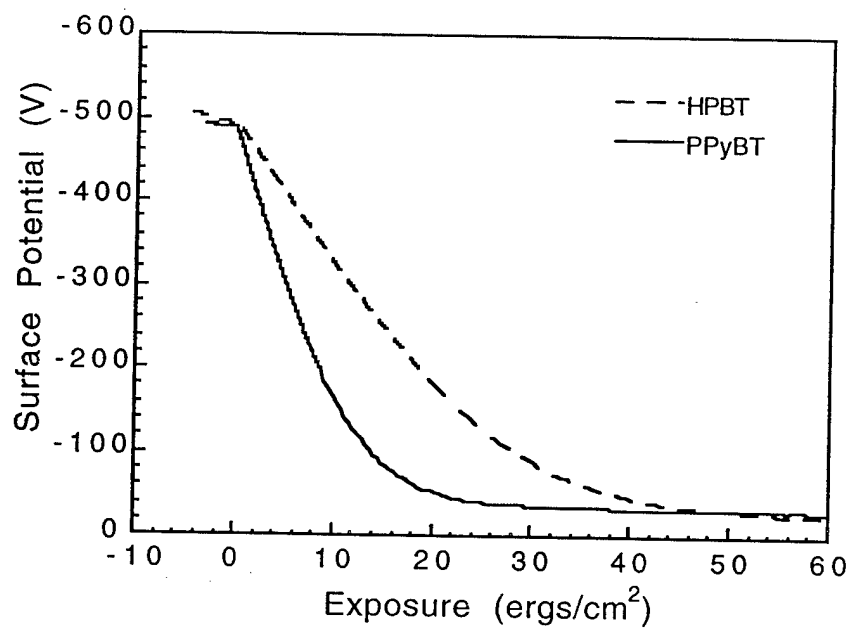


Figure 4. Photoinduced discharge curves of bilayer photoreceptors of HPBT and PPyBT.

Table 1. Photodischarge characteristics of conjugated polymer photoreceptors.

Polymer	CGL Thickness (nm)	Initial Potential (V)	Dark Decay (V/s)	Photosensitivity (ergs/cm ²)	ϕ_0	r_0 (Å)
PBZT	20	490	4.5	7.5	0.35	4.8
PBTPV	20	450	10.0	11.5	0.30	5.5
PPyBT	33	490	5.0	6.0	0.46	5.8
HPBT	80	490	10.0	15.0	0.24	4.1
BBL	20	480	2.0	18.0	0.32	4.6

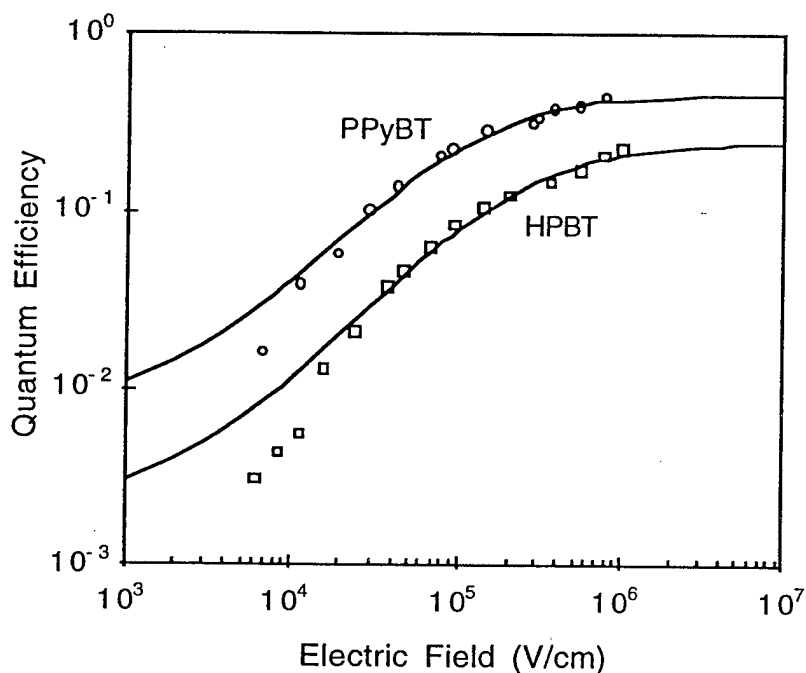


Figure 5. Charge photogeneration quantum efficiency dependence on electric field: (a) PPyBT/TTA (33-nm PPyBT, 470-nm illumination); (b) HPBT/TTA (80-nm HPBT, 480-nm illumination).

Charge photogeneration quantum efficiency of the bilayer photoreceptors were also obtained from the photodischarge measurements at electric fields of $\sim 10^4$ to $\sim 10^6$ V/cm. Figure 5 shows typical results for PPyBT/TTA and HPBT/TTA devices whose photoinduced discharge curves were shown in Figure 4. The quantum efficiency for photogeneration is a strong function of the electric field, $\phi(E)$, increasing with increasing electric field. At high electric field close to 10^6 V/cm, PBZT/TTA, PBTPV/TTA, PPyBT/TTA, HPBT/TTA, and BBL/TTA photoreceptors, whose photodischarge properties are listed in Table 1, had quantum efficiencies of 34%, 29%, 44%, 23%, and 21%, respectively.

The above results for the bilayer photoreceptors show that the photocarrier generation efficiency $\phi(E)$ varies greatly with the conjugated polymer used as the CGL since the CTL material, TTA:PC was constant. Many factors, such as electronic structure and morphology of the conjugated polymer and the film

thickness of the CGL, can be expected to influence the photocarrier generation efficiency. As will be discussed later, $\phi(E)$ can be greatly influenced by the polymer film thickness due to size effects. However, even in the case of PBZT, PBTPV, and BBL, which all have the same film thickness (20 nm, Table 1), $\phi(E)$ varies significantly and implies that the origin of the differences in charge photogeneration must ultimately be traced to the electronic structures of the polymers. It is interesting that the 2,5-pyridylene-linked polymer, PPyBT, has by far the highest quantum yield for photogeneration at any electric field. Particularly remarkable is the large difference in $\phi(E)$ between PPyBT and the 1,4-phenylene-linked polymer PBZT. The major difference in the electronic structures of these two benzobisthiazole polymers is that PPyBT has a higher electron affinity by ~ 0.2 eV.^{20(d)} To further elucidate the observed photocarrier generation properties of conjugated polymer-based photoreceptors we examine the interaction between the polymers and TTA at the bilayer interface.

Our laboratory has previously investigated the nature of charge photogeneration in triarylamine/conjugated polymer bilayer photoreceptor devices.⁶⁻⁹ On the basis of several different experiments, including optical absorption spectroscopy, wavelength-dependent photogeneration quantum yield, steady-state photoluminescence, picosecond transient absorption spectroscopy, and time-resolved fluorescence measurements, it was established that the photogeneration was *extrinsic* in nature. Specifically, it was shown that charge photogeneration occurred at the TTA/conjugated polymer bilayer interface where photoinduced exciplex formation occurred and followed by field-assisted dissociation of the exciplex.⁶⁻⁹ A schematic illustration of the exciplex model is shown in Figure 6. The conjugated polymer electron acceptor (A) when excited to its singlet excited state $^1A^*$ may relax to the ground state either radiatively (via excimer emission⁸) or nonradiatively, or can form an exciplex with the electron donor (D) molecule TTA via electron transfer. The resulting exciplex ($D-A$ or electron-hole pair) can dissociate into free charge carriers under the influence of an electric field with the rate constant $k_d(E)$, or deactivate to the ground state via radiative or nonradiative decay with the total rate constant k_f . The rate constant for electron and hole recombination is k_r .

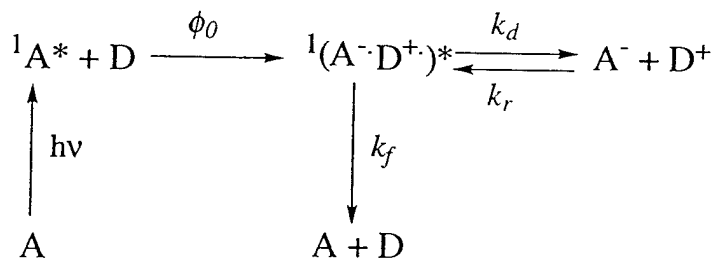


Figure 6. Schematic of exciplex-mediated charge photogeneration in conjugated polymer photoreceptors.

The exciplex-mediated charge photogeneration model can be combined with Onsager's theory to better understand the photoconductive properties of conjugated polymer photoreceptors. Electric field-dependent photogeneration quantum efficiency data for organic photoreceptors²³ have sometimes been analyzed by Onsager's 1938 theory.²⁴ This theory, however, predicts thermalized ion-pair separation distances of 20–30 Å. Also, the theory in most cases, does not predict the temperature dependence of the quantum efficiency $\phi(E)$. Theoretical kinetic models^{25,26} derived from Onsager's 1934 theory¹⁹ have been shown to give improved predictions of field and temperature dependence of quantum yield of photogeneration. We have recently developed a version of the kinetic model of charge photogeneration for application to exciplex-mediated carrier photogeneration in conjugated polymer systems where ion-pair separation distances are expected to be significantly less than 20–30 Å. In this theoretical model, the field-dependent quantum efficiency $\phi(E)$ is written as the product of the primary ion-pair ($D-A$ exciplex) quantum yield ϕ_0 which is assumed to be field-independent and the field-dependent probability for geminate ion-pair dissociation $P(E, r_0)$:¹⁸

$$\phi(E) = \phi_0 P(E, r_0) \quad (2)$$

where r_0 is the ion-pair or donor-acceptor separation distance. The two physical parameters in equation (2) can be obtained by fitting the experimental $\phi(E)$ data.¹⁸

The results of theoretical fit of $\phi(E)$ data are exemplified by those for PPyBT/TTA and HPBT/TTA devices as shown in Figure 5. The solid lines in the figure represent the calculated results from the model and the two parameters ϕ_0 and r_0 . Figure 5 shows that the experimental data and the theoretical curves are in good agreement. The ion-pair primary quantum yield ϕ_0 that was obtained is 0.46 for PPyBT/TTA and 0.24 for HPBT/TTA. The ion-pair separation distance r_0 that best fits the data was 5.8 Å for PPyBT and 4.1 Å for HPBT/TTA. The ϕ_0 and r_0 values for all the conjugated polymer/TTA devices are listed in Table 1. Ion-pair (donor-acceptor) separation distance of 4–6 Å obtained in the conjugated polymer/TTA bilayer systems (Table 1) is very realistic and is in the range of what can be expected for donor-acceptor separation distances in intermolecular exciplexes.²⁷ The primary ion-pair quantum yield in these bilayer photoreceptors was in the range of 0.24 to 0.46. The order of decreasing primary quantum yield ϕ_0 in the series of conjugated polymers in Table 1 is PPyBT > PBZT > BBL > PBTPV > HPBT. There is no obvious correlation of ϕ_0 with the electron affinities of the polymers,^{20(b)} suggesting that a more detailed investigation of the ground state and excited state electronic structures of conjugated polymers will be essential to elucidate the structure- ϕ_0 relationships.

Nanoscale Size Effects on Photoreceptors. We have previously reported nanoscale size effects on PPyBT/TTA bilayer photoreceptors.⁹ A 3-fold increase in quantum efficiency of photogeneration was observed when the conjugated polymer layer (CGL) thickness was reduced from ~100 to ~10 nm. Our results showed that the primary quantum yield ϕ_0 of ion-pairs (D–A exciplexes) obtained from the theoretical fit of equation (2) to the experimental $\phi(E)$ data is 0.22, 0.21, 0.45, 0.46, and 0.62 for PPyBT thickness of 195, 97, 43, 33, and 9 nm, respectively. The photosensitivity of PPyBT/TTA photoreceptors also varies with film thickness of the CGL. In contrast, the most probable ion-pair (donor-acceptor) separation distance obtained from the fit was constant at about 6 Å (5.9 Å for 9 nm, 5.8 Å for 33 nm, 5.8 Å for 43 nm, 6.0 Å for 97 nm, and 5.8 Å for 195 nm) regardless of the PPyBT film thickness. The origin of these nanoscale size effects is intimately connected with the extrinsic nature of charge photogeneration in these bilayer photoreceptors. First, the interfacial interaction (exciplex formation) between the conjugated polymer and TTA is maximized in thinner films. However, because of the small exciton diffusion length of the PPyBT only a fraction ϕ_0 of excitons created diffuses to the interface region and results in the formation of the ion-pair species (exciplexes). Exciton diffusion lengths of conjugated polymers are generally in the range of 5–20 nm which is much less than their absorption depths.^{7,28} For example, the exciton diffusion length of PBZT films was 10–18 nm.⁷ A value of about 5 nm has been reported for poly(*p*-phenylenevinylene) (PPV) films.²⁸ We expect the exciton diffusion length of PPyBT films to be about the same order of magnitude as PBZT and PPV, i.e. ~5–18 nm. Such a small exciton diffusion length in PPyBT inhibits the formation of ion-pairs (exciplexes) when the film is very thick. Thus, the closer is the conjugated polymer layer thickness to the exciton diffusion length the larger the expected ϕ_0 . These nanoscale size effects in conjugated polymer photoreceptors underlay the need for control of the film thickness of the CGL as well as the opportunity to enhance the performance of organic photoreceptors through nanoscale fabrication.

Polymer Blend Photoreceptors. Our exploration of blends of conjugated polymers as CGL materials in organic photoreceptors was motivated by the results of recent studies of the photophysical properties of binary blends of π -conjugated polymers in our laboratory.^{29–33} It was found that binary blends of conjugated polymers such as those in Figure 1 were miscible over the entire composition range or phase-separated on the nanometer scale, resulting in materials with novel properties not shown by the component homopolymers.^{29–33} Among the novel features observed in such binary blends are: spectral modulation of optical absorption with blend composition,²⁹ photoinduced electron transfer,²⁹ efficient energy transfer,³⁰ bipolar charge transport,^{20(f)} enhanced electroluminescence,³¹ enhanced nonlinear optical properties,³² and quantum confinement effects.³³ The finding that the optical absorption spectra of binary blends of BBL:PBZT and BBL:HPBT were simple composition averages of those of the components²⁹ suggests that as CGL materials they could extend the spectral range of photosensitivity to 300–700 nm (see Figure 3). Similarly, observation of photoinduced electron transfer in the same binary polymer blends suggests a possible means of enhancing charge photogeneration in photoreceptors.

Figure 7 shows the optical absorption spectrum of a 80-nm thin film of a 50-mol% BBL:PBZT blend. As expected, the rather broad absorption in the range 300-700 nm is composed of the characteristic absorption bands of BBL and PBZT. The more intense absorption in the 420-480 nm spectral range reflects the greater absorption coefficient of the PBZT component.²⁹ The spectral sensitivity of a 50% BBL:PBZT blend photoreceptor (80-nm thick CGL), characterized by the ratio of initial photodischarge rate to incident light intensity which is proportional to the charge photogeneration quantum efficiency (see equation (1)), is also shown in Figure 7. The spectral response of charge photogeneration tracks the absorption spectrum very well (Figure 7), demonstrating that the blends of conjugated polymers provide a facile means of tuning the spectral sensitivity of organic photoelectronic devices.

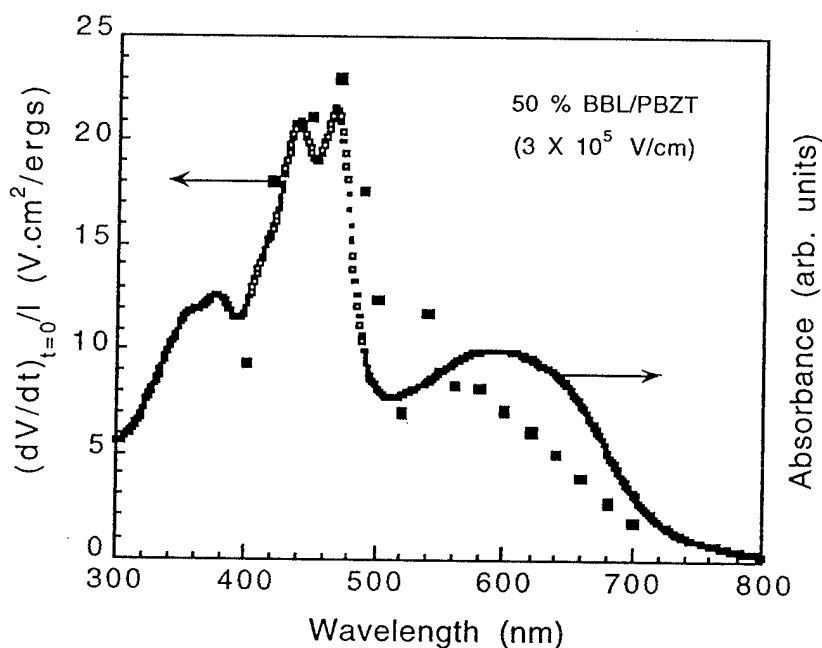


Figure 7. Spectral response of charge photogeneration in a 50-mol% BBL:PBZT blend photoreceptor and the blend absorption spectrum.

Figure 8 shows the field-dependent charge photogeneration quantum efficiency $\phi(E)$ of a 50-nm thick BBL:PBZT (10 mol% BBL)/TTA photoreceptor along with similar data for the pure homopolymer photoreceptors (20-nm thick PBZT and 20-nm thick BBL). In spite of the possible size effects favoring the homopolymer-based photoreceptors with thinner CGL, the 10% blend photoreceptor has quantum yield $\phi(E)$ that is comparable to the pure PBZT device at electric fields below 10^5 V/cm. At higher fields ($>10^5$ V/cm), the 10% blend has superior carrier photogeneration yields. At 5×10^5 V/cm, for example, the 10% blend photoreceptor has a 45% quantum efficiency compared to 32% for the pure PBZT device and only 18% for the pure BBL device. This represents factors of 1.41 and 2.50 enhancements of charge photogeneration in the polymer blend device compared to those of the two homopolymer devices. Although the detail mechanism of this enhancement of charge photogeneration in conjugated polymer blend photoreceptors is yet to be established, it is likely related to the observed photoinduced electron transfer in such blends²⁹ which may increase the effective exciton diffusion length in the charge generation layer.

CONCLUSIONS

Xerographic photoreceptors made from conjugated polymer thin film charge generation layers have been found to exhibit low dark decay, good photosensitivity over a wide spectral range in the visible, and high photocarrier generation efficiency which are comparable or superior to current organic photoreceptors. In addition, the excellent thermal stability and mechanical properties of conjugated polymer thin films and the relative ease of fabricating bilayer photoreceptors from them suggest that they are very promising for electrophotographic imaging and related optoelectronic applications. The observed nanoscale size effects on the performance of bilayer photoreceptors is related to both the *extrinsic* nature of charge photogeneration in the devices and the small exciton diffusion lengths in conjugated polymers. Thus the photocarrier generation efficiency of bilayer organic photoreceptors can be significantly enhanced if the CGL thickness is reduced to the nanoscale range and is comparable to the exciton diffusion length. The results of our study of charge photogeneration in binary blends of conjugated polymers show that they exhibit enhanced photocarrier generation efficiency as well as enhanced spectral range of photosensitivity compared to the component homopolymers.

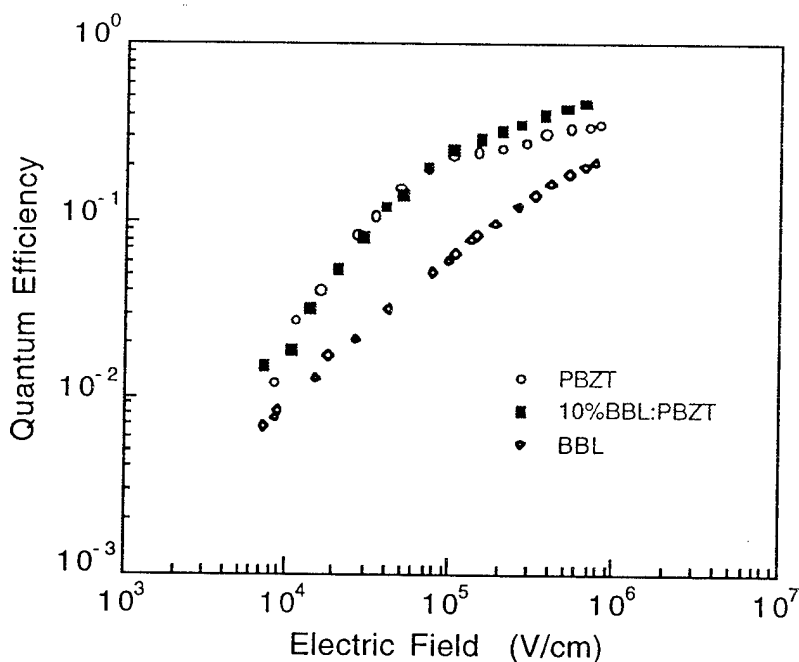


Figure 8. Charge photogeneration quantum efficiency dependence on electric field: BBL/TTA (20-nm BBL, 565-nm illumination); PBZT/TTA (20-nm PBZT, 470-nm illumination); and 10, mol% BBL:PBZT blend/TTA (50-nm thick, 470-nm illumination).

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (CTS-9311741, CHE-9120001) and the Office of Naval Research. We thank Eastman Kodak Company for samples of TTA.

REFERENCES

1. P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Imaging Systems*, Marcel Dekker, New York, 1993.
2. K.-Y. Law, "Organic photoconductive materials: recent trends and developments", *Chem. Rev.* **93**, pp.449-486, 1993.
3. P. M. Borsenberger, "Hole transport in tris-p-tolylamine-doped bisphenol-A-polycarbonate", *J. Appl. Phys.* **68**, pp.6263-6273, 1990.
4. P. M. Borsenberger, E. H. Magin, and J. J. Fitzgerald, "Concentration dependence of the hole mobility of 1,1-bis(di-4-tolylamino)cyclohexane (TAPC) dope polystyrene (PS)", *J. Phys. Chem.* **97**, pp.9213-9216, 1993.
5. A. R. Melnyk and D. M. Pai, "Organic photoreceptors: an overview", *Proc. SPIE-Int. Soc. Opt. Eng.* **1253**, pp.141-153, 1990.
6. J. A. Osaheni, S. A. Jenekhe, and J. Perlstein, "Efficient photogeneration of charge carriers in a layered photoreceptor using a conjugated polymer", *Appl. Phys. Lett.* **64**, pp.3112-3114, 1994.
7. J. A. Osaheni, S. A. Jenekhe, and J. Perlstein, "Photogeneration of charge carriers in bilayer assemblies of conjugated rigid-rod polymers", *J. Phys. Chem.* **98**, pp.12727-12736, 1994.
8. S. A. Jenekhe and J. A. Osaheni, "Excimers and exciplexes of conjugated polymers", *Science* **265**, pp.765-768, 1994.
9. X. Zhang, S. A. Jenekhe, and J. Perlstein, "Nanoscale size effects on photoconductivity of semiconducting polymer films", *Chem. Mater.* **8**, pp.1571-1574, 1996.
10. (a) N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky, and F. Wudl, "Semiconducting polymer-buckminsterfullerene heterojunctions: diodes, photodiodes, and photovoltaic cells", *Appl. Phys. Lett.* **62**, pp.585-587, 1993. (b) H. Antoniadis, B. R. Hsieh, M. A. Abkowitz, S. A. Jenekhe, and M. Stolka, "Photovoltaic and photoconductive properties of aluminum/poly(p-phenylene vinylene) interfaces", *Synth. Met.* **62**, pp.265-271, 1994. (c) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, "Light-emitting diodes based on conjugated polymers", *Nature* **347**, pp.539-541, 1990.
11. L. Lauchlan, S. Etemad, T. C. Chung, A. J. Heeger, and A. G. MacDiarmid, "Photoexcitations in polyacetylene", *Phys. Rev. B* **24**, pp.3701-3711, 1981.
12. (a) D. Moses, M. Sinclair, and A. J. Heeger, "Carrier photogeneration and mobility in polydiacetylene: fast transient photoconductivity", *Phys. Rev. Lett.* **58**, 2710-2713, 1987. (b) T. Ravindran, W. H. Kim, A. K. Jain, J. Kumar, and S. K. Tripathy, "Steady-state photoconductivity in a novel solution-cast polydiacetylene film", *Synth. Met.* **66**, pp.203-207, 1994.
13. (a) G. Yu, K. Pakbaz, and A. J. Heeger, "Semiconducting polymer diodes: large size, low cost photodetectors with excellent visible-ultraviolet sensitivity", *Appl. Phys. Lett.* **64**, pp.3492-3494, 1994. (b) M. Gailberger and H. Bassler, "dc and transient photoconductivity of poly(2-phenyl-1,4-phenylenevinylene)", *Phys. Rev. B* **44**, pp.8643-8651, 1991.
14. G. Yu, S. D. Phillips, H. Tomozawa, and A. J. Heeger, "Subnanosecond transient photoconductivity in poly(3-hexylthiophene)", *Phys. Rev. B* **42**, pp.3004-3010, 1990.
15. M. A. Abkowitz, M. Stolka, H. Antoniadis, A. K. Agrawal, S. A. Jenekhe, "Photoconductivity in conjugated rigid-rod polyquinolines", *Solid State Commun.* **83**, pp.937-941, 1992.
16. (a) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, "Photoinduced electron transfer from a conducting polymer to buckminsterfullerene", *Science* **258**, pp.1474-1476, 1992. (b) C. H. Lee, G. Yu, D. Moses, K. Pakbaz, C. Zhang, N. S. Sariciftci, A. J. Heeger, and F. Wudl, "Sensitization of the photoconductivity of conducting polymers by C₆₀: photoinduced electron transfer", *Phys. Rev. B* **48**, pp.15425-15433, 1993. (c) K. Yoshino, X. H. Yin, S. Morina, T. Kawai, and A. A. Zakhidov, "Enhanced photoconductivity of doped poly(3-alkylthiophene)", *Solid State Commun.* **85**, pp.85-88, 1993. (d) S. Morina, A. A. Zakhidov, and K. Yoshino, "Doping effect of buckminsterfullerene in conducting polymers: change of absorption spectrum and quenching of luminescence", *Solid State Commun.* **82**, pp.249-252, 1992. (e) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, "Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor

- heterojunctions", *Science* **270**, pp.1789-1791, 1995. (f) G. Yu and A. J. Heeger, "Charge separation and photovoltaic conversion in polymer composites with internal donor/acceptor heterojunctions", *J. Appl. Phys.* **78**, pp.4510-4515, 1995.
17. J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, "Efficient photodiode from interpenetrating polymer networks", *Nature* **376**, pp.498-500, 1995.
 18. X. Zhang, S. A. Jenekhe, and J. Perlstein, "Modeling of exciplex-mediated charge photogeneration in conjugated polymer-based bilayer photoreceptors", manuscript in preparation.
 19. L. Onsager, "Deviation from Ohm's law in weak electrolytes", *J. Chem. Phys.* **2**, pp.599-615, 1934.
 20. (a) J. A. Osaheni and S. A. Jenekhe, "Synthesis and processing of heterocyclic polymers as electronic, optoelectronic, and nonlinear optical materials. 1. New conjugated rigid rod benzobisthiazole polymers", *Chem. Mater.* **4**, pp.1282-1290, 1992. (b) J. A. Osaheni, PhD Thesis, University of Rochester, 1994. (c) J. A. Osaheni and S. A. Jenekhe, "New red light-emitting conjugated rigid-rod polymer: poly(benzobisthiazole-1,4-phenylenebisvinylene)", *Macromolecules* **26**, pp.4726-4728, 1993 (d) A. K. Alanko, MS Thesis, University of Rochester, 1995. (e) A. K. Alanko and S. A. Jenekhe, manuscript in preparation. (f) R. M. Tarkka X. Zhang, and S. A. Jenekhe, "Electrically generated intramolecular proton transfer: electroluminescence and stimulated emission from polymers", *J. Am. Chem. Soc.* **118**, pp.9438-9439, 1996. (g) X. L. Chen and S. A. Jenekhe, "Bipolar conducting polymers: blends of p-type polypyrrole and n-type ladder polymer", *Macromolecules* **30**, pp.1728-1733, 1997.
 21. (a) S. A. Jenekhe, P. O. Johnson, and A. K. Agrawal, "Solubilization, solutions, and processing of aromatic heterocyclic rigid rod polymers in aprotic solvents: poly(p-phenylene-2,6-benzobisthiazole)", *Macromolecules* **22**, pp.3216-3222, 1989. (b) S. A. Jenekhe and P. O. Johnson, "Complexation-mediated solubilization and processing of rigid-chain and ladder polymers in aprotic organic solvents", *Macromolecules* **23**, pp.4419-4429, 1990.
 22. J. Mort and D. Pai, Eds., *Photoconductivity and Related Phenomena*, Chapter 11, Elsevier, New York, 1976.
 23. P. M. Borsenberger, L. E. Contois, and D. C. Hoesterey, "Hole photogeneration in binary solid solutions of triphenylamine and bisphenol-A-polycarbonate", *J. Chem. Phys.* **68**, pp.637-641, 1978.
 24. L. Onsager, "Initial recombination of ions", *Phys. Rev.* **54**, pp.554-557, 1938.
 25. T. E. Goliber and J. H. Perlstein, "Analysis of photogeneration in a doped polymer system in terms of a kinetic model for electric-field-assisted dissociation of charge-transfer states", *J. Chem. Phys.* **80**, pp.4162-4167, 1984.
 26. C. H. Braun, "Electric field assisted dissociation of charge transfer states as a mechanism of photocarrier production", *J. Chem. Phys.* **80**, pp.4157-4161, 1984.
 27. M. A. Winnik, Ed., *Photophysical and Photochemical Tools in Polymer Science*, pp.24, Reidel, Dordrecht, Holland, 1986.
 28. M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, "Defect quenching of conjugated polymer luminescence", *Phys. Rev. Lett.* **73**, pp.744-747, 1994.
 29. S. A. Jenekhe, L. R. de Paor, X. L. Chen, and R. M. Tarkka, "Photoinduced electron transfer in binary blends of conjugated polymers", *Chem. Mater.* **8**, pp.2401-2404, 1996.
 30. C.-J. Yang and S. A. Jenekhe, "Electronic energy transfer in new polymer nanocomposite assemblies", *Supramol. Sci.* **1**, pp.91-101, 1994.
 31. X. Zhang, D. M. Kale, and S. A. Jenekhe, "Blends of conjugated polymers. 4. Enhanced electroluminescence of binary blends of polyquinolines", *Macromolecules*, submitted.
 32. S. A. Jenekhe et.al., manuscript in preparation.
 33. (a) X. L. Chen and S. A. Jenekhe, "Block conjugated copolymers: toward quantum-well nanostructures for exploring spatial confinement effects on electronic, optoelectronic and optical phenomena", *Macromolecules* **29**, pp.6189-6192, 1996. (b) X. L. Chen and S. A. Jenekhe, "Semiconducting polymer quantum wires", *Appl. Phys. Lett.* **70**, pp.487-489, 1997.